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JAPANESE KOKAI PATENT, HEI 8-165357

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TITLE OF INVENTION : Heat-shrinkable Sheet or Film

APPLICATION NO. AND DATE : HEI 6-311033, December 14, 1994

INVENTORS : S. Nishijima, et al.

**APPLICANT : Mitsui Petrochemical Industries K.K.[000005887]
Tokyo, Japan**

NUMBER OF CLAIMS : 3

REQUEST FOR EXAMINATION : None

Abstract

[Constitution] Heat-shrinkable sheet or film, prepared by biaxially stretching at least one type of cycloolefin resin selected from the group comprising [I-1], [I-2], [I-3], and [I-4] described below. [I-1] : Ethylene/cycloolefin random copolymer obtained by copolymerizing ethylene and cycloolefins represented by a specified formula. [I-2] : Polymer or copolymer obtained by opening the ring of the above-said cycloolefins. [I-3] : Hydrogenated products of the opening polymer or copolymer described above in [I-2]. [I-4] : Grafted product from [I-1], [I-2], or [I-3].

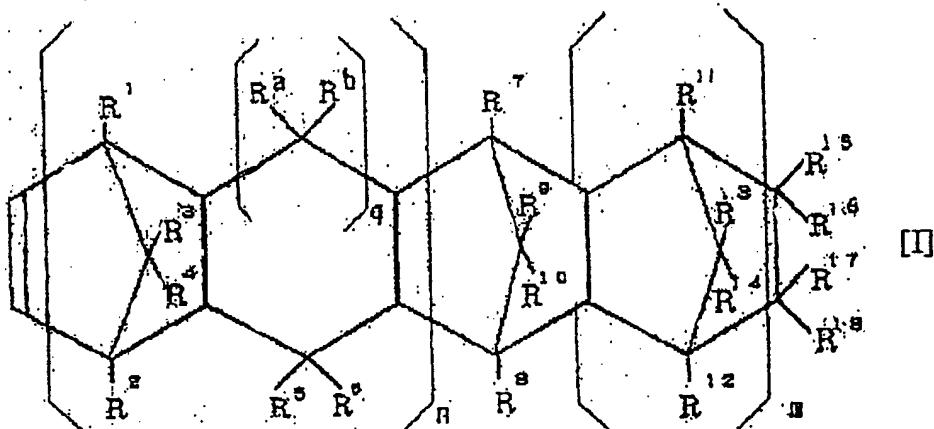
[Effect] Heat-shrinkable sheet or film having excellent shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, and transparency, and high rigidity, and can be inserted easily with the content when it is used as a heat-shrinkable film, is provided.

Claims

[Claim 1] [A] Heat-shrinkable sheet or film, acquired by biaxially stretching at least one type of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3], and [I-4] described below.

[I-1] : Ethylene/cycloolefin random copolymers, obtained by copolymerizing ethylene and cycloolefins represented by the following formula [I] or [II].

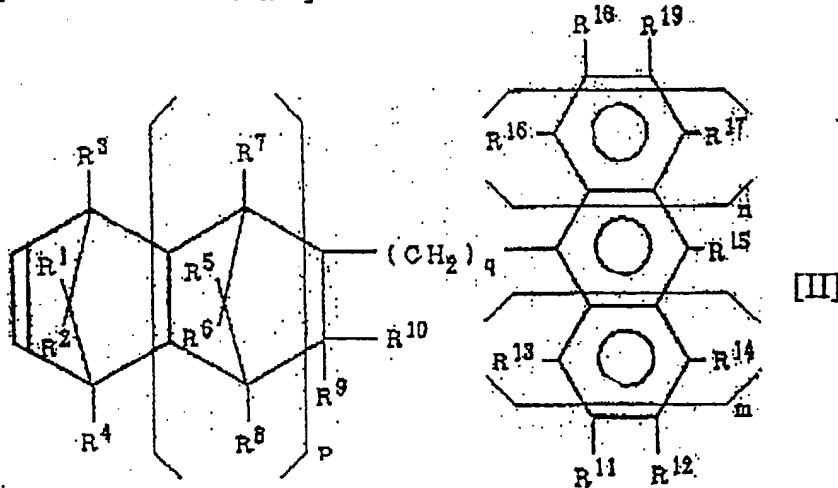
[Chemical formula 1]



[where, n is 0 or 1, m is 0 or a positive integer, q is 0 or 1,
R¹ - R¹⁸ and R^a and R^b are, independently, hydrogen atom, halogen atom or a hydrocarbon group, R¹⁶ - R¹⁸ may bind mutually to form

a single ring or multiple ring and the single ring or multiple ring may have double bond(s), and R¹⁶ and R¹⁸ or R¹⁷ and R¹⁸ may form an alkylidene group]

[Chemical formula 2]



[where, p and q is 0 or an integer of 1 or higher, m and n are 0, 1, or 2, R¹ - R¹⁹ are, independently, hydrogen atom, halogen atom, aliphatic hydrocarbon group, alicyclic hydrocarbon group, aromatic hydrocarbon group, or alkoxy group, the carbon atom linked to the R⁹(^m) (or R¹⁰) may link with the carbon atom linked to the R¹³(ⁿ) and R¹¹ directly or through a C₁ - C₃ alkylene group, and if n = m = 0, the R¹⁶(^m) and R¹⁸(ⁿ) or R¹⁵ and R¹⁹ may link mutually to form a mononuclear or polynuclear aromatic ring]

[I-2] : Polymers or copolymers obtained by opening the ring of the cycloolefins represented by [I] or [II].

[I-3] : Hydrogenated products of the polymers or copolymer obtained by opening the ring of the above-said [I-2].

[I-4] : Grafted products derived from the above-said [I-1], [I-2] or [I-3].

[Claim 2] Heat-shrinkable sheet or film, acquired by biaxially stretching the cycloolefin resin composition comprising

[A] at least one type of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3] and [I-4], and

[B] at least one type of soft polymer selected from (i) - (v).

(i) Soft cycloolefin copolymer having a limit viscosity $[\eta]$ (measured in decalin at 135°C) of 0.01 - 10 dl/g and a glass transition temperature (Tg) of 0°C or lower, formed from ethylene, α -olefins other than ethylene, and cycloolefins represented by the above-described formula [I] or [II]; (ii) amorphous or low crystallinity α -olefin copolymers having a glass transition temperature (Tg) of 0°C or lower, formed from at least two types of α -olefins; (iii) α -olefin/diene copolymers having a glass transition temperature (Tg) of 0°C or lower, formed from at least two types of α -olefins and at least one type of unconjugated diene; (iv) aromatic vinyl hydrocarbon/conjugated diene random or block copolymers or its hydrogenated products, having a glass transition temperature (Tg) of 0°C or lower; and (v) soft polymers formed from isobutylene or soft copolymers formed from isobutylene and conjugated diene.

[Claim 3] Heat-shrinkable sheet or film, obtained by biaxially stretching the laminate formed from

[A] at least one type of the layer of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3], and [I-4], and

[B] at least one type of soft polymer selected from a group comprising (i) - (v).

Comprehensive explanation of invention

[0001]

[Technological field of invention]

This invention relates to heat-shrinkable sheets or films made of cycloolefin polymer and soft polymer. More particularly, this invention relates to heat-shrinkable sheets or films that have excellent shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, and transparency, and also has high rigidity and can be inserted with the content easily when it is used as a heat-shrinkable film.

[0002]

[Technical background of invention]

Earlier, the present inventors have discovered that the cycloolefin polymer sheet or film acquired by biaxially stretching the [A] cycloolefin random copolymers having a limit viscosity $[\eta]$ (measured in decalin at 135°C) of 0.01 - 10 dl/g and softening temperature (TMA) of 70°C or higher, formed from ethylene component and a cycloolefin component represented by a specified formula (example : 8-ethyl-tetracyclo[4,4,0,1^{2,5},1^{7,10}]-3-dodecene, or the ring-opened polymer made of at least one

type of olefin component selected from the cycloolefins represented by the above-said specified formula, or its hydrogenated products have excellent transparency, waterproofness and heat shrinkability and so on, and such sheet or film has been disclosed previously in Japanese Kokai Patent, HEI 2-196832 (1990).

[0003]

However, further extensive study has revealed that the biaxially stretched product formed from a combination of the cycloolefin resin such as the above-said cycloolefin random polymer and another different polymer has excellent shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, transparency and high rigidity and can be inserted with the content easily when it is used as a heat-shrinkable film. Based on this discovery, the present inventors have finally perfected this invention.

[0004]

And, the present applicant has discovered also that a sheet or a film made from ring-opened polymers or ring-opened copolymers derived from the cycloolefins represented by a specified formula, hydrogenated products of such polymers or copolymer, and at least one type of cycloolefin resin having a limit viscosity $[\eta]$ of 0.01 - 10 dl/g and a softening temperature of 70°C or higher, selected from a group comprising the addition polymer made of ethylene and cycloolefins represented by a specified formula, and a certain soft polymer, shows excellent tearability and gas barrier property, etc., and such discovery has been disclosed in our Japanese Patent Application HEI 2-289637 (1990). Even though this Japanese Patent Application HEI 2-289637 (1990) discloses that the thus-obtained biaxially stretched film or sheet excels in heat-sealability and transparency, there is no mentioning about the heat-shrinkability of the film (or sheet).

[0005]

[Object of invention]

The object of this invention is to provide a heat-shrinkable sheet or film which has excellent shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, and high rigidity and can be inserted easily with the content when it is used as a heat-shrinkable sheet or film.

[0006]

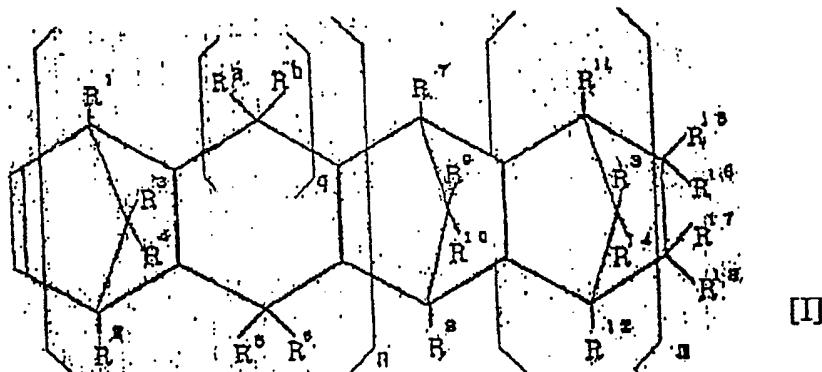
[Scope of invention]

[A] The characteristic of the first heat-shrinkable sheet or film of this invention is that it is prepared by biaxially stretching at least one type of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3], and [I-4] described below.

[I-1] Ethylene/cycloolefin random copolymer obtained by copolymerizing ethylene and a cycloolefin represented by the following formula [I] or [II].

[0007]

[Chemical formula 3]

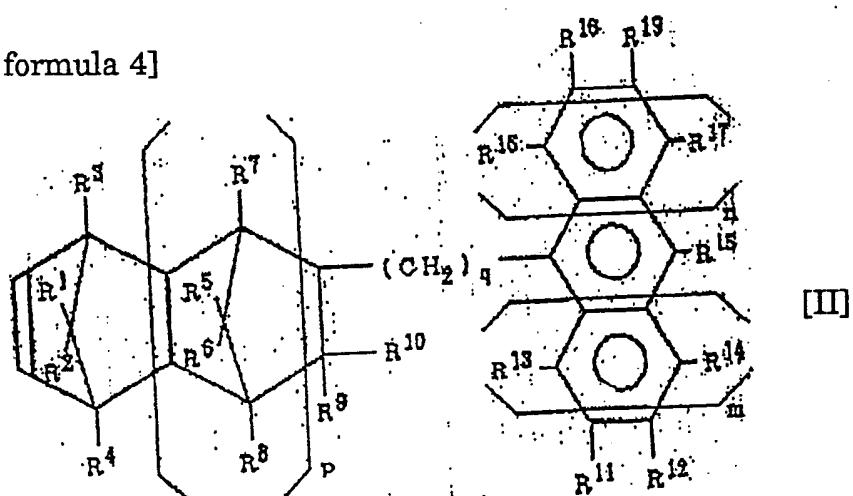


[0008]

In the formula [I], n is 0 or 1, m is 0 or a positive integer, q is 0 or 1, R¹ - R¹⁸ and R^a - R^b are, independently, hydrogen atom, halogen atom or hydrocarbon group, R¹⁶ - R¹⁸ may bind mutually to form a single ring or multiple rings and the single ring or multiple ring may have double bond(s), and R¹⁵ and R¹⁶ or R¹⁷ and R¹⁸ may form an alkylidene group.

[0009]

[Chemical formula 4]



[0010]

In the formula [II], p and q is 0 or an integer of 1 or higher, m and n are 0, 1, or 2, R¹ - R¹⁹ are, independently, hydrogen atom, halogen atom, aliphatic hydrocarbon group, alicyclic hydrocarbon group, aromatic hydrocarbon group, or alkoxy group, the carbon atom linked to the R⁹ (or R¹⁰) may be linked to the carbon atom linked to the R¹⁰ - R¹¹ directly or through a C₁ - C₃ alkylene group, and if n = m = 0, the R^{16(?)} and R^{18(?)} or R¹⁵ and R¹⁹ may link mutually to form a mononuclear or polynuclear aromatic ring. [I-2] Open-ring polymers or copolymers obtained by opening the ring of the cycloolefins represented by [I] or [II]. [I-3] Hydrogenated products of the open-ring polymers or copolymers described above. [I-4] Grafted products derived from the above-said [I-1], [I-2], or [I-3].

[0011]

The second heat-shrinkable sheet or film of this invention, acquired by biaxially stretching the cycloolefin resin composition, comprises

- [A] at least one type of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3] and [I-4], and
- [B] at least one type of soft polymer selected from (i) - (v).

[0012]

(i) Soft cycloolefin copolymer having a limit viscosity [η] (measured in decalin at 135°C) of 0.01 - 10 dl/g and a glass transition temperature (Tg) of 0°C or lower, formed from ethylene, α-olefins other than ethylene, and cycloolefins represented by the above-described formula [I] or [II]; (ii) amorphous or low crystallinity α-olefin copolymers having a glass transition temperature (Tg) of 0°C or lower, formed from at least two types of α-olefins; (iii) α-olefin/diene copolymers having a glass transition temperature (Tg) of 0°C or lower, formed from at least two types of α-olefins and at least one type of unconjugated diene; (iv) aromatic vinyl hydrocarbon/conjugated diene random or block copolymers or its hydrogenated products, having a glass transition temperature (Tg) of 0°C or lower; and (v) soft polymers formed from isobutylene or soft copolymers formed from isobutylene and conjugated diene.

[0013]

The third heat-shrinkable sheet or film of this invention is acquired by biaxially stretching the laminate formed from

- [A] at least one type of the layer of cycloolefin resin selected from a group comprising [I-1], [I-2], [I-3], and [I-4], and

[B] at least one type of soft polymer selected from a group comprising (i) - (v).

[0014]

The heat-shrinkable sheet or film of this invention excels in shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, and transparency, and has high rigidity and can be inserted easily with a content when it is used as a heat-shrinkable film.

[0015]

[Explanation of invention]

The heat-shrinkable sheet or film of this invention is explained embodied in the following.

[0016]

The first heat-shrinkable sheet or film of this invention is formed by biaxially stretching at least one type of cycloolefin resin [A] ("cycloolefin resin [A]", hereinafter) selected from a group comprising [I-1], [I-2], [I-3], and [I-4].

[0017]

The second heat-shrinkable sheet or film of this invention is formed by biaxially stretching the cycloolefin resin composition that contains the above-said cycloolefin resin [A] and at least one type of soft polymer [B] ("soft polymer [B]", hereinafter) selected from the group comprising (i) - (v).

[0018]

If the above-said α -olefin copolymer (ii), from among the following soft polymers, is used, the second heat-shrinkable sheet or film of this invention will have a particularly excellent film impact, and tends to excel in the balance of shrinking properties, transparency, tensile strength, tear strength, gas permeability, and water vapor permeability.

[0019]

The third heat-shrinkable sheet or film of this invention is formed by biaxially stretching the laminate that is formed from a layer made of the cycloolefin resin [A] (cycloolefin resin layer) and a layer made of the soft polymer [B] (soft polymer layer).

[0020]

At this point, let us explain the cycloolefin resin [A].

[A] Cycloolefin resins

At least one type of polymer selected from [I-1] (random copolymers of ethylene and the cycloolefin represented by the following formula [I] or [II]), [I-2] (open-ring polymers or copolymers of cycloolefins represented by the following formula [I] or [II]), [I-3] (hydrogenated products of the above-said open-ring polymers or copolymers [I-2]), and [I-4] (grafted products of the above-said [I-1], [I-2], or [I-3]), can be used as the cycloolefin resin [A] in this invention.

[0021]

Generally, the cycloolefin resin [A] to be used in this invention is amorphous or low in crystallinity, and the degree of crystallization, determined by X-ray diffraction method, is 20% or lower, preferably 10% or lower.

[0022]

Limit viscosity $[\eta]$ of the cycloolefin resin [A], measured in decalin at 135°C, is 0.01 - 20 dl/g, preferably 0.03 - 10 dl/g. And, 0.05 - 8 dl/g is even more desirable.

[0023]

Iodine value of such cycloolefin resin [A] is normally 5 or lower, and majority of them is 1 or lower. And, even when the melting point of the cycloolefin resin is tested by using a differential scanning calorimeter (DSC), often the melting point can not be detected.

[0024]

Another property of such cycloolefin resin is its high glass transition temperature (Tg) and high softening temperature (TMA). Glass transition temperature (Tg) is in 50 - 230°C range, and in majority of cases it is in 70 - 210°C range. With such cycloolefins, the softening temperature of the acquired cycloolefin resin composition (which will be mentioned later) exists at 70°C or higher, preferably in 70 - 250°C range, and more preferably in 90 - 250°C range. And, 90 - 230°C is even more desirable. And, in majority of cases, it is in 100 - 200°C range.

[0025]

Thermal decomposition temperature of the cycloolefin resins is in 350 - 420°C range, mainly in 370 - 400°C range. As to the mechanical properties, flexural rupture ratio is normally in 1×10^4 - 5×10^4 kg/cm² range, and the bending strength is normally in 300 - 1500 kg/cm² range.

[0026]

The density is in 0.86 - 1.10 g/cm³ range, and mainly in 0.88 - 1.08 g/cm³ range. And, refractive index (ASTM D542) is 1.47 - 1.58, mainly in 1.48 - 1.56 range. And, since this cycloolefin resin is substantially amorphous as mentioned above, it has low haze (ASTM D1003) and has high transparency.

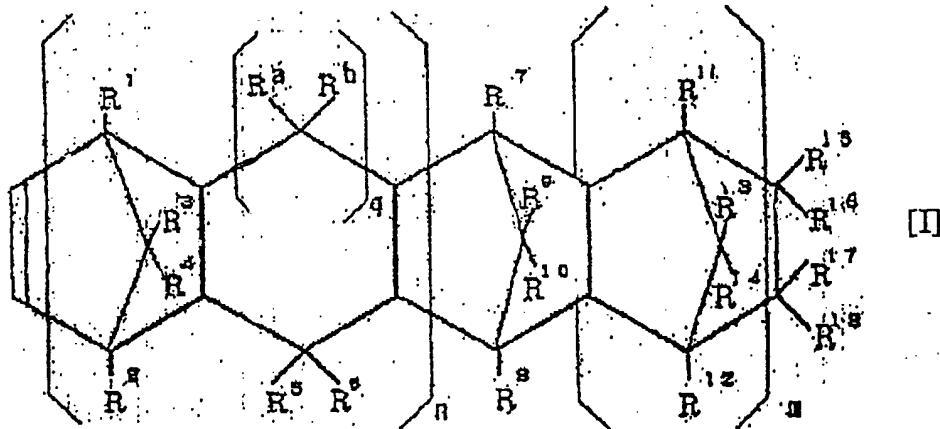
[0027]

At this point, let us explain the cycloolefins represented by the formula [I] or [II] that forms the cycloolefin resin [A] to be used in this invention.

Cycloolefins

[0028]

[Chemical formula 5]



[0029]

In the above formula [I], n is 0 or 1, m is 0 or a positive integer, and q is 0 or 1. Incidentally, if q is 1, the R^a and R^b are, independently, the following atoms or hydrocarbon groups, and if q is 0, each of their bonds link to form a five-membered ring.

[0030]

$R^1 - R^{18}$ and R^a and R^b are, independently, hydrogen atoms, halogen atom or hydrocarbon group. In this case, halogen atoms are fluorine atom, chlorine atom, bromine atom or iodine atom.

[0031]

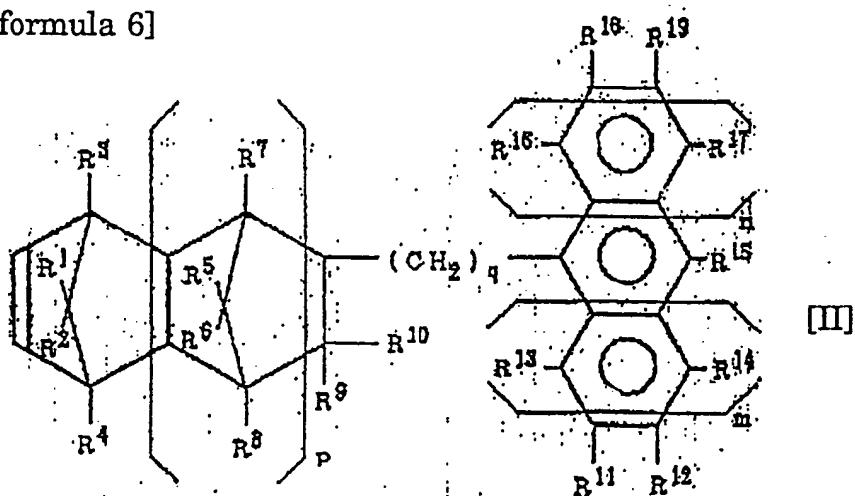
And, $C_1 - C_{20}$ alkyl groups, $C_3 - C_{15}$ cycloalkyl groups, and aromatic hydrocarbon groups can be mentioned as the examples of hydrocarbon groups. Examples of alkyl group are methyl group, ethyl group, propyl group, isopropyl group, amyl group, hexyl group, octyl group, decyl group, dodecyl group and octadecyl group. An example of cycloalkyl group is cyclohexyl group. And, examples of aromatic hydrocarbon group are phenyl group and naphthyl group and so on.

[0032]

These hydrocarbon groups may be substituted by halogen atom. And, in the above-said formula [I], the $R^{15(?)}$ - $R^{18(?)}$ may link mutually to form a single ring or multiple rings. And, the thus-formed single ring or multiple ring may have double bond(s). Examples of the thus-formed single ring or multiple ring are illustrated in the following.

[0033]

[Chemical formula 6]



[0034]

In the formula [III], p and q are 0 or a positive integer, m and n are 0, 1, or 2. And, $R^1 - R^{19}$ are, independently, hydrogen atom, halogen atom, hydrocarbon group or alkoxy group.

[0035]

The halogen atoms are the same as the halogen atoms in the above-said formula [I]. And examples of hydrocarbon group are $C_1 - C_{20}$ alkyl groups, $C_1 - C_{20}$ halogenated alkyl groups, $C_3 - C_{15}$ cycloalkyl groups or aromatic hydrocarbon groups. Examples of alkyl group are methyl group, ethyl group, propyl group, isopropyl group, amyl group, hexyl group, octyl group, decyl group, dodecyl group and octadecyl group.

An example of cycloalkyl group is cyclohexyl group. And, examples of aromatic hydrocarbon groups are aryl group and aralkyl groups such as phenyl group, tolyl group, naphthyl group, benzyl group and phenylethyl group and so on.

[0036]

Methoxy group, ethoxy group and propoxy group and so on can be mentioned as the examples of alkoxy group. These hydrocarbon groups and alkoxy groups may be substituted by fluorine atom, chlorine atom, bromine atom or iodine atom.

[0037]

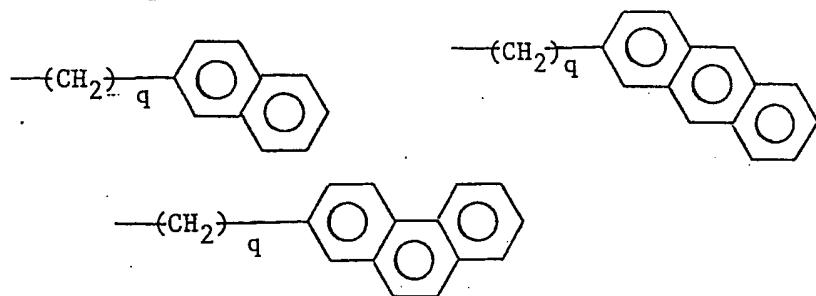
And, the carbon atom bound to the $R^{9(7)} - C^{10}$ and the carbon atom bound to the $R^{18(7)}$ or the carbon atom bound to R^{11} may be linked together directly or through a $C_1 - C_3$ alkylene group. Thus, if the two carbon atoms are linked together through an alkylene group, the groups represented by $R^{9(7)}$ and $R^{18(7)}$ or the groups represented by $R^{10(7)}$ and $R^{11(7)}$ are joined together to form an alkylene group such as ethylene group ($-CH_2CH_2-$) or propylene group ($-CH_2CH_2CH_2-$).

[0038]

And, if $n = m = 0$, R^{16} and $R^{18(7)}$ or R^{15} and R^{19} may be linked mutually to form a mononuclear or polynuclear aromatic ring. In this case, an aromatic ring formed from $R^{16(7)}$ and $R^{12(7)}$ at $n = m = 0$ can be mentioned as the example of the mononuclear or polynuclear aromatic ring, as indicated in the following.

[0039]

[Chemical formula 7]

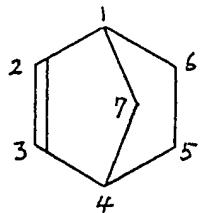


[0040]

In the above structures, q has the same meaning as the q in the formula [II]. Examples of the cycloolefins represented by the above-described formula [I] or [II] are shown in the following.

[0041]

[Chemical formula 8]



[0042]

Bicyclo[2.2.1]-2-heptene (= norbornene) illustrated in the above formula (the number 1 - 7 shown in the above formula represents the position of the carbon) and the derivatives formed by substituting a hydrocarbon group in the compound.

[0043]

Examples of the hydrocarbon group are 5-methyl, 5,6-dimethyl, 1-methyl, 5-ethyl, 5-n-butyl, 5-isobutyl, 7-methyl, 5-phenyl, 5-methyl-5-phenyl, 5-benzyl, 5-tolyl, 5-(ethylphenyl), 5-(isopropylphenyl), 5-(biphenyl), 5-(β -naphthyl), 5-(α -naphthyl), 5-anthracenyl, and 5,6-diphenyl groups.

[0044]

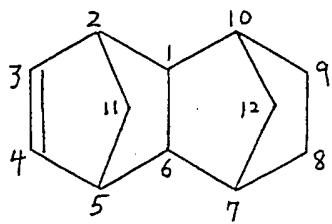
Examples of other derivatives are bicyclo[2.2.1]-2-heptene derivatives such as cyclopentadiene/acenaphthylene addition product, 1,4-methano-1,4,4a,9a-tetrahydro-fluorene, 1,4-methano-1,4,4a,5,10,10a-hexahydro-anthracene and so on.

[0045]

Other examples are tricyclo[4.3.0.1^{2,5}]-3-decene derivatives such as tricyclo[4.3.0.1^{1,5}]-3-decene, 2-methyl-tricyclo[4.3.0.1^{2,5}]-3-decene, and 5-methyl-tricyclo[4.3.0.1^{2,5}]-3-decene, and tricyclo[4.4.,0.1^{2,5}]-3-undecene derivatives such as tricyclo[4.4.0.1^{2,5}]-3-undecene and 10-methyl-tricyclo[4.4.0.1^{2,5}]-3-undecene and so on.

[0046]

[Chemical formula 9]



[0047]

Tetracyclo[4,4,0,1^{2,5},1^{7,10}]-3-dodecenes and the derivatives formed by substituting a hydrocarbon group in the compound. Examples of the hydrocarbon group are 8-methyl, 8-ethyl, 8-propyl, 8-butyl, 8-isobutyl, 8-hexyl, 8-cyclohexyl, 8-stearyl, 5,10-dimethyl, 2,10-dimethyl, 8,9-dimethyl, 8-ethyl-9-methyl, 11,12-dimethyl, 2,7,9-trimethyl, 2,7-dimethyl-9-ethyl, 9-isobutyl-2,7-dimethyl, 9,11,12-trimethyl, 9-ethyl-11,12-dimethyl, 9-isobutyl-11,12-dimethyl, 5,8,9,10-tetramethyl, 8-ethylidene, 8-ethylidene-9-methyl, 8-ethylidene-9-ethyl, 8-ethylidene-9-isopropyl, 8-ethylidene-9-butyl, 8-n-propylidene, 8-n-propylidene-9-methyl, 8-n-propylidene-9-ethyl, 8-n-propylidene-9-methyl, 8-n-propylidene-9-isopropyl, 8-n-propylidene-9-butyl, 8-isopropylidene, 8-isopropylidene-9-methyl, 8-isopropylidene-9-ethyl, 8-isopropylidene-isopropyl, 8-isopropylidene-9-butyl, 8-chloro, 8-bromo, 8-fluoro, 8,9-dichloro, 8-phenyl, 8-methyl-8-phenyl, 8-benzyl, 8-tolyl, 8-(ethylphenyl), 8-(isopropylphenyl), 8,9-diphenyl, 8-(biphenyl), 8-(β -naphthyl), 8-(α -naphthyl), 8-(anthracenyl), 5,6-diphenyl groups and so on.

[0048]

Other examples are tetracyclo[4,4,0,1^{2,5},1^{7,10}]-3-dodecene derivatives such as the addition product formed from (cyclopentadiene/acenaphthylene addition product) and cyclopentadiene; pentacyclo[6,5,1,1^{3,6},0^{2,7},0^{9(?)},13^(?)]-pentadecene and its derivatives; pentacyclo[7,4,0,1^{2,5},1^{9(?)},12^(?),0^{8(?)},13^(?)]-3-pentadecene and its derivatives; pentacyclo[8,4,0,1^{2,5},1^{9,12(?)},0^{8,13}]-hexadecene and its derivatives; pentacyclo[6,6,1,1^{3,6},0^{2,5(?)},0^{9,14}]-4-hexadecene and its derivatives; hexacyclo[6,6,1,1^{3,6(?)},1^{10,13},0^{2,7},0^{9,14}]-heptadecene and its derivatives; heptacyclo[8,7,0,1^{3,5},1^{10,17},1^{12,15},0^{11,16(?)}]-4-eicocene and its derivatives; heptacyclo[8,8,0,1^{2,9},1^{4,7},1^{11,13},0^{3,8},0^{12,17(?)}]-5-heneicocene and its derivatives; octacyclo[8,8,0,1^{2,9},1^{4,7},1^{11,15},1^{13,16},0^{12,17}]-5-dococene and its derivatives; and nonacyclo[10,9,1,1^{4(?)},7,1^{13(?)},20,1^{16(?)},18,0^{2(?)},10,0^{3(?)},5,0^{14,19}]-5-pentacocene and its derivatives.

[0049]

Examples of the cycloolefins represented by the afore-said formula [I] or [II] that can be used in this invention are described above. More specific structures of these compounds are illustrated in [0032] - [0053] of the Specification of the Japanese Patent Application HEI 5-196475 (1993) filed earlier by the present applicant. And, the examples illustrated can be used as the cycloolefins in the invention of this application.

[0050]

The cycloolefins represented by the general formula [I] or [II] can be prepared by reacting a cyclopentadiene with an olefin that has a corresponding structure, by Diels-Adler reaction.

[0051]

Each of these cycloolefins may be used alone or two or more such cycloolefins may be combined and used together. The cycloolefin resins to be used in this invention can be prepared from the cycloolefins represented in the above-said formula [I] or [II], using the method proposed earlier by the present applicant in, for example, Japanese Kokai Patent SHO 60-168708(1985), Japanese Kokai Patent SHO 61-120816 (1986), Japanese Kokai Patent SHO 61-115912 (1986), Japanese Kokai Patent SHO 61-115916 (1986), Japanese Kokai Patent SHO 61-271308 (1986), Japanese Kokai Patent SHO 61-272216 (1986), Japanese Kokai Patent SHO 62-252406 (1987), and Japanese Kokai Patent SHO 62-252407 (1987), by selecting a proper condition.

[0052]

[I-1] Ethylene/cycloolefin random copolymer

Ethylene/cycloolefin random copolymer [I-1] contains 20 - 95 mol %, preferably 30 - 90 mol %, of the structural unit derived from ethylene and 5 - 80 mol %, preferably 10 - 70 mol %, of the structural unit derived from cycloolefin. Incidentally, compositional ratio of ethylene and cycloolefin is determined by C¹³-NMR analysis.

[0053]

In this ethylene/cycloolefin random copolymer [I-1], the structural unit derived from ethylene and the structural unit derived from cycloolefin are arranged and linked randomly, to form a substantially linear structure. That this copolymer is substantially linear and does not have a gel-like crosslinked structure can be confirmed by the absence of insoluble material in the solution when the copolymer

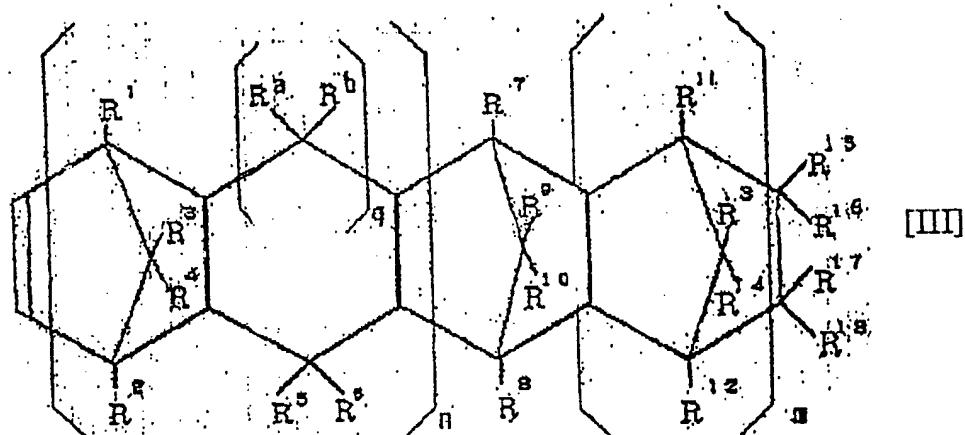
is dissolved in organic solvent. For example, one can confirm this fact by complete dissolution of the copolymer in decalin at 135°C during measurement of the limit viscosity $[\eta]$.

[0054]

In the ethylene/cycloolefin random copolymer [I-1] to be used in this invention, at least a part of the cycloolefin represented by the formula [I] or [II] is believed to form a repeating unit represented by the following formula [III] or [IV].

[0055]

[Chemical formula 10]

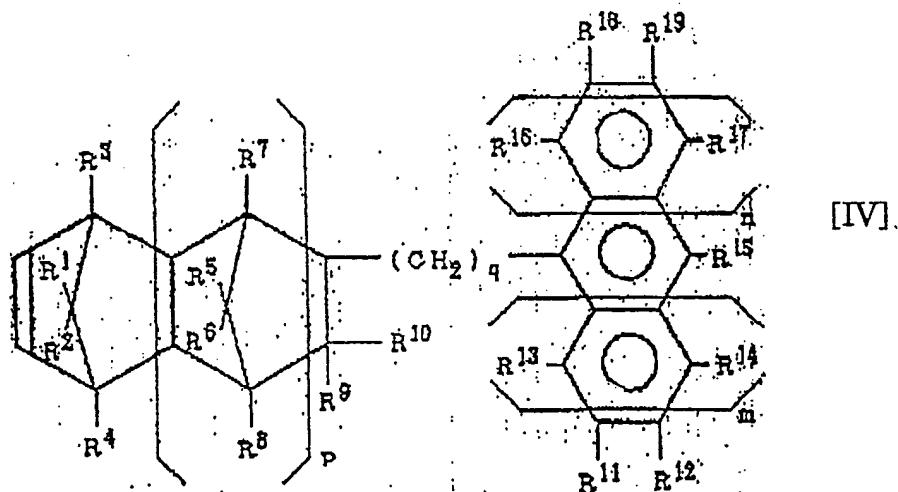


[0056]

In the formula [III], n, m, q, R¹ - R¹⁸ and R^a and R^b have the same meaning as in the formula [I].

[0057]

[Chemical formula 11]



[0058]

In the formula [IV], n, m, p, q and $R^1 - R^{19}$ have the same meaning as in the formula [III]. And, the ethylene/cycloolefin random copolymer [I-1] to be used in this invention may have a structural unit derived from other copolymerizable monomers, as long as it does not interfere with the purpose of this invention.

[0059]

Olefins other than the above-said ethylene or cycloolefin can be mentioned as the other monomers. Examples are $C_3 - C_{20}$ α -olefins such as propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicocene and so on; cycloolefins such as cyclobutene, cyclopentene, cyclohexene, 3,4-dimethyl-cyclopentene, 3-methyl-cyclohexene, 2-(2-methylbutyl)-1-cyclohexene, and cyclooctene, and 3a,5,6,7a-tetrahydro-4,7-methano-1H-indene and so on; and unconjugated dienes such as 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,7-octadiene, dicyclopentadiene and 5-vinyl-2-norbornene and so on.

[0060]

Each of these other monomers may be used alone or they may be combined and used together. In the ethylene/cycloolefin random copolymer [I-1], content of the

structural unit derived from other monomers is normally 20 mol % or less, preferably 10 mol % or less.

[0061]

The ethylene/cycloolefin random copolymer [I-1] to be used in this invention can be prepared by any of the production processes disclosed in the above-described publications, using ethylene and the cycloolefins represented by the formula [I-] or [II]. Among them, the preferred method is the production method of ethylene/cycloolefin random copolymer [I-1], that run the copolymerization in a hydrocarbon solvent and uses the catalyst formed from the hydrocarbon solvent-soluble vanadium compound and organoaluminum compound as the catalyst.

[0062]

And, a solid metallocene catalyst of the IV-B family can be used also in this copolymerization reaction. This solid metallocene catalyst of IV-B family is a catalyst made of a transition metal compound containing a ligand having cyclopentadienyl skeleton, organoaluminuomoxy compound, and if necessary an organoaluminum compound. Examples of the transition metal of VI (?) family are zirconium, titanium or hafnium, and these transition metals have a ligand that contains at least one cyclopentadienyl skeleton. Examples of the ligand that contains cyclopentadienyl skeleton are cyclopentadienyl group that may be substituted by alkyl group, indenyl group, tetrahydroindenyl group, and fluorenyl group. These groups may be linked through another group such as alkylene group and so on. Examples of the ligand other than the ligand that contains cyclopentadienyl skeleton are alkyl group, cycloalkyl group, aryl group, and aralkyl group and so on.

[0063]

Those which are used for production of olefin resins can be used as the organoaluminuomoxy compound and organoaluminum compound. Such solid metallocene catalysts of IV-B family have been described, for example, in Japanese Kokai Patent SHO 61-221206 (1986), Japanese Kokai Patent SHO 64-106 (1984), and Japanese Kokai Patent HEI 2-173112 (1990) and so on.

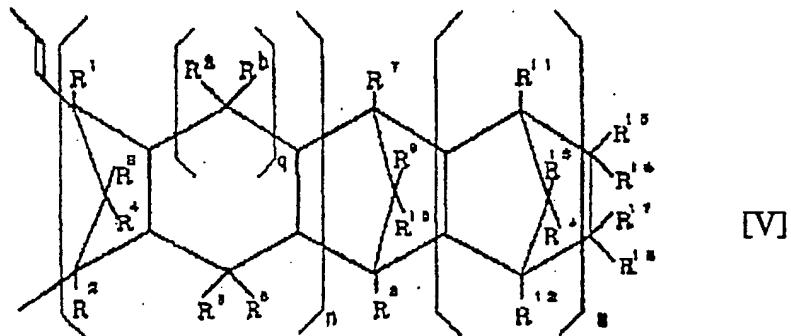
[0064]

[I-2] Open-ring polymers or open-ring copolymers of cycloolefins

In the open ring polymers or open-ring copolymers of cycloolefins, at least a part of the cycloolefins represented by the above-said formula [I] or [II] is believed to form a repeating unit represented by the following formula [V] or [VI].

[0065]

[Chemical formula 12]

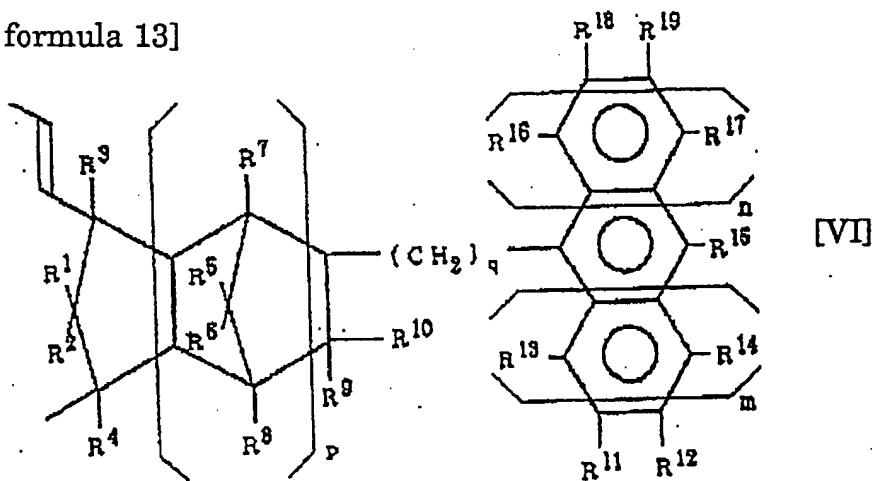


[0066]

In the formula [V], n, m, q and R¹ - R¹⁹, and R^a - R^b have the same meaning as the formula [I].

[00067]

[Chemical formula 13]



[0068]

In the formula [VI], n, m, p, q, and R¹ - R¹⁹ have the same meaning as the formula [II]. Such open-ring polymers or open-ring copolymers can be prepared by the production method disclosed in the above-described publications. For example, they can be prepared by polymerizing or copolymerizing the cycloolefins represented by the above-described formula [I] in the presence of a ring-opening polymerization catalyst.

[0069]

Examples of such ring-opening polymerization catalyst are the catalysts made of the halides, nitrates or acetylacetones of the metals selected from ruthenium, rhodium, palladium, osmium, indium and platinum, and a reducing agent, or the catalysts made from halides or acetylacetone of the metals selected from titanium, palladium, zirconium or molybdenum, and organoaluminum compound.

[0070]

[I-3] Hydrogenated products of open-ring polymers or copolymers

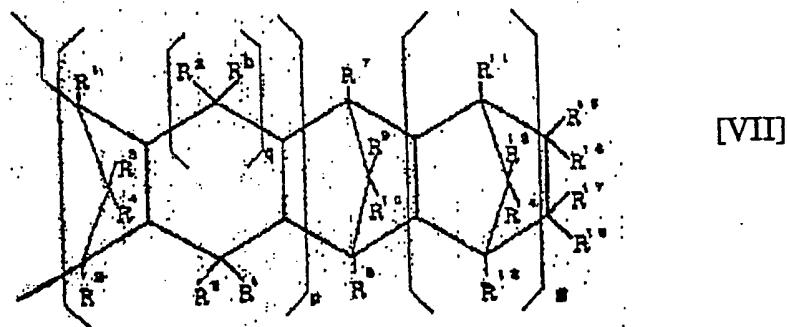
Hydrogenated products of the open-ring copolymers or copolymer [I-3] to be used in this invention can be obtained by hydrogenating the thus-obtained open ring polymer or copolymer [I-2] in the presence of a known hydrogenation catalyst.

[0071]

In these hydrogenated products of the open ring polymer or copolymer, at least a part of the cycloolefins represented by the formula [I] or [II] is believed to have a repeating unit represented by the following formula [VII] or [VIII].

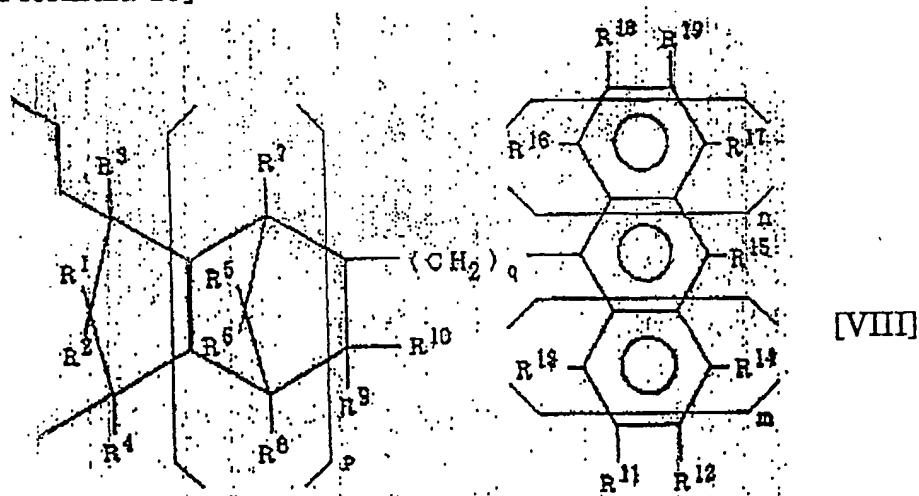
[0072]

[Chemical formula 14]



[0074]

[Chemical formula 15]



[0075]

In the formula [VIII], n, m, p, q, and R¹ - R¹⁹ have the same meaning as the formula [II].

[I-4] Grafted products

Grafted products of the cycloolefin resin are the grafted products obtained from the above-described ethylene/cycloolefin random copolymers [I-1], open ring polymers or copolymers of the cycloolefins [I-2], or the grafted products of the hydrogenated products of open-ring polymers or copolymer [I-3].

[0076]

Normally, unsaturated carboxylic acids are used as the modifying agent. Examples are unsaturated carboxylic acids such as (meth)acrylic acids, maleic acid, fumaric acid, tetrahydrophthalic acid, itaconic acid, citraconic acid, crotonic acid, isocrotonic acid, endo-cis-bicyclo[2.2.1]hepto-5-ene-2,3-dicarboxylic acid (Nadic acidTM), and derivatives of such unsaturated carboxylic acids such as unsaturated carboxylic anhydride, unsaturated carboxylic halides, unsaturated carboxylamides, unsaturated carboxylimides, unsaturated carboxylate esters and so on.

[0077]

Examples of the derivatives of unsaturated carboxylic acids are maleic anhydride, citraconic anhydride, malenyl chloride, maleimide, monomethyl maleate, dimethyl maleate, glycidyl maleate and so on.

[0078]

Among these modifying agents, α,β -unsaturated dicarboxylic acids and anhydrides of α,β -unsaturated dicarboxylic acids, such as maleic acid, nadic acid and their anhydrides are used favorably. And, a combination of two or more such modifying agents may be used also.

[0079]

Normally, the desirable graft ratio in the grafted products of cycloolefin resin to be used in this invention is 10 mol % or lower. The grafted products of such cycloolefin resin may be prepared by adding the modifying agent to the cycloolefin resin to create a desired graft ratio and then graft polymerizing the mixture, or a grafted product with a high graft ratio may be prepared and then this grafted product may be mixed with an unmodified cycloolefin resin.

[0080]

In order to obtain a grafted product of cycloolefin resin from a cycloolefin resin and a modifying agent, polymer grafting methods known in the prior art can be used. For example, grafted product can be obtained by adding a modifying agent to the cycloolefin resin melt and then running the graft-polymerization reaction, or by adding a modifying agent to the solution of cycloolefin resin and running a graft reaction.

[0081]

Such graft reaction is carried out normally at 60 - 350°C. And, the graft reaction may be carried out in the presence of a radical initiator such as organic peroxide and azo compound.

[0082]

And, the modified products having the above-described graft ratio can be obtained directly by running a graft reaction of cycloolefin resin and modifying agent. Or, after obtaining a modified product having a high graft ratio by running a graft reaction of cycloolefin resin and the modifying agent, the modified product may be diluted with an unmodified cycloolefin resin to create a desired graft ratio.

[0083]

In the present invention, each of the above-described [I-1], [I-2], [I-3], and [I-4] can be used alone as the cycloolefin resin [A]. And, their combination may be used also.

[0084]

Among these, ethylene/cycloolefin random copolymers [I-1] are used favorably. In this invention, a resin composition prepared by adding other resins to this cycloolefin resin [A] may be used also. Thus, a variety of polymers is blended with the above-said cycloolefin resin [A] to form a so-called "polymer alloy" in which the other resin is dispersed in the cycloolefin resin, and then this "polymer alloy" is stretched biaxially to form a film. Examples of the polymers (resin component) that can form a "polymer alloy" together with the cycloolefin resin are given in the following. In the second heat-shrinkable sheet or film of this invention, the "polymers (1) derived from hydrocarbons having one or two unsaturated bonds" (polyolefins) described in the following, or the "soft polymer (17)" described in the following are preferred. Furthermore, the " α -olefinic copolymers (ii)" described in the following are favored because they excel in film impact, and have a good balance of shrinking property, transparency, tensile strength, tear strength, gas permeability and water vapor permeability.

[0085]

And, in the third heat-shrinkable sheet or film of this invention, polyamides, ethylene/vinyl alcohol copolymers, ethylene/vinyl acetate copolymers (EVA), polyvinylidene chloride (PVDE), and polyolefins are used favorably as the other resin which is to be laminated with the cycloolefin resin [A].

[0086]

Other resin components that may be added

(1) Polymers derived from hydrocarbons having one or two unsaturated bonds.

Examples are polyolefins such as polyethylene, polypropylene, polymethyl-butene-1, poly-4-methyl-pentene-1, polybutene-1, and polystyrene and so on. And, these polyolefins may have a crosslinked structure.

(2) Halogen-containing vinyl polymers.

[0087]

Examples are polyvinylchloride, polyvinylidenechloride, polyvinylfluoride, polychloroprene, and chlorinated rubber and so on.

(3) Polymers derived from α,β -unsaturated acids and the derivatives derived from such acids.

[0088]

Examples are polyacrylates, polymethacrylates, polyacrylamides, polyacrylonitriles, or the copolymers formed from the monomers that constitute the above-said polymers, such as acrylonitrile/butadiene/styrene copolymers, acrylonitrile/styrene copolymers, acrylonitrile/styrene/acrylate ester copolymers and so on.

(4) Polymers of unsaturated alcohols and amines and the polymers derived from its acyl derivatives or acetal.

[0089]

Examples are polyvinyl alcohols, polyvinyl acetates, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate, polyallyl melamine, or the copolymers of the monomers that constitute the above-said polymers such as ethylene/vinyl acetate copolymers and so on.

(5) Polymers derived from epoxides.

[0090]

Examples are polyethylenoxide or the polymers derived from bisglycidyl ether, and so on.

(6) Polyacetals.

[0091]

Examples are polyoxymethylene, polyoxyethylene and polyoxymethylenes that contain ethylenoxide as the comonomer.

(7) Polyphenyleneoxide.

(8) Polycarbonates.

(9) Polysulfones.

(10) Polyurethanes and urea resins.

(11) Polyamides and copolyamides derived from diamine and dicarboxylic acid and/or aminocarboxylic acid or the corresponding lactams.

[0092]

Examples are Nylon 6, Nylon 66, Nylon 11, and Nylon 12 and so on.

(12) Polyesters derived from dicarboxylic acids and dialcohols and/or oxycarboxylic acids or the corresponding lactones.

[0093]

Examples are polyester terephthalates, polybutylene terephthalate, poly-1,4-dimethylol cyclohexane terephthalate and so on.

(13) Crosslinked polymers derived from aldehyde and phenol, urea or melamine.

[0094]

Examples are phenol/formaldehyde resins, urea/formaldehyde resins, melamine/formaldehyde resins and so on.

(14) Alkyd resins.

[0095]

Examples are glycerin/phthalic acid resin and so on.

(15) Unsaturated polyester resins, derived from the copolymers of saturated and unsaturated dicarboxylic acids and polyvalent alcohols and using vinyl compound as the crosslinking agent, and modified resins that contain halogens.

(16) Natural polymers.

[0096]

Examples are cellulose, rubber, proteins or their derivatives such as acetylcellulose, propionylcellulose, cellulose ethers and so on.

(17) Soft polymers.

[0097]

Examples of the soft polymer are rubber-like component selected from the group comprising (i) - (v). And, the cycloolefin resin composition made of the cycloolefin resin [A] and such rubber-like components excels particularly in impact strength (film

impact). These rubber-like components may be crosslinked in the presence of an organic peroxide. Rubber-like components crosslinked with organic peroxide are preferred because it can yield a heat-shrinkable sheet or film with excellent impact resistance (film impact).

[0098]

Soft polymers which are used favorably in this invention are explained in the following.

[Soft polymers (i) containing cycloolefin component]

The soft polymers that contain cycloolefin component are the copolymers that can be obtained by copolymerizing ethylene component and the cycloolefin (formula [I] or formula [II]) component which is identical to the one used for preparation of the above-described cycloolefin resins. Beside containing cycloolefin component and ethylene component as the essential components, this soft polymer (i) may contain appropriate amount of α -olefin component.

[0099]

Examples of α -olefin are propylene, 1-butene, 4-methyl-1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicocene and so on. Among them, C_3 - C_{20} α -olefins are preferred. And, cycloolefins and cyclodienes such as norbornene, ethylidene norbornene and dichloropentadiene and so on are favored also.

[0100]

In the soft polymer (i) containing cycloolefin component, content of ethylene component is 40 - 98 mol %, preferably 50 - 90 mol %. Content of α -olefin component is 2 - 50 mol %, and content of cycloolefin component is 2 - 20 mol %, preferably 2 - 15 mol %.

[0101]

Unlike the above-described cycloolefin resin, the glass transition temperature (T_g) of the soft polymer (i) is 0°C or lower, preferably -10°C or lower; and the limit viscosity $[\eta]$, measured in decalin at 135°C, is 0.01 - 10 dl/g, preferably 0.8 - 7 dl/g. Degree of crystallization of the soft polymer (i), measured by X-ray diffraction method, is 0 - 10%, preferably 0 - 7%, and 0 - 5% is particularly desirable.

[0102]

The soft polymer (i) can be prepared under a properly selected condition, following the method proposed earlier by the present applicants in Japanese Kokai Patent SHO 60-168708 (1985), Japanese Kokai Patent SHO 61-120816 (1986), Japanese Kokai Patent SHO 61-115912 (1986), Japanese Kokai Patent SHO 61-115916 (1986), Japanese Kokai Patent SHO 61-271308 (1986), Japanese Kokai Patent SHO 61-272216 (1986), Japanese Kokai Patent SHO 62-252406 (1987) and Japanese Kokai Patent SHO 62-252406 (1987).

[0103]

[α -Olefin copolymers (ii)]

The α -olefin copolymer (ii) which is used as the soft polymer is made from at least two types of α -olefins, and is an amorphous copolymer or a copolymer having low crystallinity. Examples are ethylene/ α -olefin copolymers and propylene/ α -olefin copolymers.

[0104]

Normally, C_3 - C_{20} α -olefins are used as the α -olefins to constitute the ethylene/ α -olefin copolymer. Examples are propylene, 1-butene, 4-methyl-1-butene, 1-hexene, 1-octene and 1-decene or their mixtures. Among them, C_3 - C_{10} α -olefins are particularly desirable.

[0105]

Even though the ethylene/ α -olefin mol ratio in the ethylene/ α -olefin copolymer may differ with the types of α -olefin, but normally it is 40/60 - 95/5. And, if the α -olefin is propylene, preferred mol ratio is 40/60 - 90/10. And, if the α -olefin has 4 or more carbons, the preferred mol ratio is 50/50 - 95/5.

[0106]

Normally, C_4 - C_{20} α -olefins are used as the α -olefins to constitute the propylene/ α -olefin copolymers. Examples are 1-butene, 4-methyl-1-butene, 1-hexene, 1-octene and 1-decene, and their mixture. Among them, C_4 - C_{10} α -olefins are particularly desirable.

[0107]

In the above-described propylene/α-olefin copolymers, the mol ratio (propylene/α-olefin) of propylene and α-olefin may differ with the type of α-olefin, but normally it is 50/50 - 95/5.

[0108]

[α-Olefin/diene copolymers (iii)]

Examples of the α-olefin/diene copolymers (iii) that are used as the soft polymer are ethylene/α-olefin/diene copolymer rubbers and propylene/α-olefin/diene copolymer rubbers.

[0109]

$C_3 - C_{20}$ (in case of propylene/α-olefins, it is $C_4 - C_{20}$) α-olefins such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene or their mixtures can be used as the α-olefins to constitute such copolymer rubbers. Among them, $C_3 - C_{10}$ α-olefins are particularly desirable.

[0110]

Examples of the diene component to constitute the copolymer rubbers are linear unconjugated dienes such as 1,4-hexadiene, 1,6-octadiene, 2-methyl-1,5-hexadiene, 6-methyl-1,5-heptadiene, and 7-methyl-1,6-octadiene; cyclic unconjugated dienes such as cyclohexadiene, dicyclopentadiene, methyl tetrahydroindene, 5-vinyl-methylene-2-norbornene, 5-isopropylidene-2-norbornene and 6-chloromethyl-5-isopropenyl-2-norbornene; and 2,3-diisopropylidene-5-norbornene; 2-ethylidene-3-isopropylidene-5-norbornene; and 2-propenyl-2,2-norbornadiene and so on.

[0111]

In the above-described ethylene/α-olefin/diene copolymer rubbers, the mol ratio (ethylene/α-olefin) of ethylene and α-olefin may differ with the type of α-olefin, but normally it is 40/60 - 90/10.

[0112]

And, the content of the repeating unit derived from the diene component in such copolymer rubber is normally 1 - 20 mol %, preferably 2 - 15 mol %.

[Aromatic vinyl hydrocarbon/conjugated diene soft copolymers (iv)]

The aromatic vinyl hydrocarbon/conjugated diene soft copolymers to be used as the soft polymer are the random copolymers or block copolymers of aromatic vinyl hydrocarbons and conjugated dienes, or their hydrogenated products. Examples are styrene/butadiene block copolymer rubbers, styrene/butadiene/styrene block copolymer rubbers, styrene/isoprene block copolymer rubbers, styrene/isoprene/styrene block copolymer rubbers, hydrogenated styrene/butadiene/styrene block copolymer rubbers, hydrogenated styrene/isoprene/styrene block copolymer rubbers, styrene/butadiene random copolymer rubbers, or the rubbers obtained by graft-polymerizing methyl acrylate and so on.

[0113]

In these copolymer rubbers, the hydrogenated copolymer rubbers are the copolymer rubbers obtained by hydrogenating a part or entire double bond(s) remained in the above-described copolymer rubbers.

[0114]

In this invention, if the impact strength (film impact) of the heat-shrinkable sheet or film must be raised, it is desirable to use such copolymer rubbers.

[Soft polymers or copolymers (v) made of isobutylene or isobutylene/conjugated diene]

Examples of the isobutylene soft polymers or copolymers which are used as the soft polymer are polyisobutylene rubber, polyisoprene rubber, polybutadiene rubber, isobutylene/isoprene copolymer rubber and so on.

[0115]

Incidentally, property of the copolymers (ii) - (v) which are the soft polymers is nearly identical to the property of the cycloolefin polymer (i). Limit viscosity $[\eta]$, measured in decalin at 135°C, is 0.01 - 10 dl/g, preferably 0.08 - 7 dl/g, and the glass transition temperature (Tg) is 0°C or lower, preferably -10°C or lower. And, the degree of crystallization, measured by X-ray diffraction method, is 0 - 10%, preferably 0 - 7%. And, 0 - 5% is particularly desirable.

[0116]

In this invention, the above-described soft polymer (17) can be blended directly with the cycloolefin resin [A] and used for preparing the heat-shrinkable sheet or film. For example, first a blend is prepared by dispersing the soft polymer in the cycloolefin

resin, and then this blend is treated with an organic peroxide, to form crosslinkages between the soft polymer and the cycloolefin resin in the blend.

[0117]

Examples of the organic peroxide are ketone peroxides such as methylethyl ketone peroxide, cyclohexanone peroxide and so on; peroxy ketals such as 1,1-BIS(t-butylperoxy) cyclohexane, 2,2-BIS(t-butylperoxy) octane and so on; hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide and so on; dialkyl peroxides such as di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (trade name = PERHEXA 25B), 2,5-dimethyl-2,5-di(t-butylperoxy) hexene-3 and so on; diacyl peroxides such as lauroyl peroxide, benzoyl peroxide and so on; and peroxy esters such as t-butylperoxy acetate, t-butylperoxy benzoate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane and so on.

[0118]

The amount of the organic peroxide component to be added is 0.01 - 1 weight part, preferably 0.05 - 0.5 weight part, per 100 weight parts of the total combined amount of cycloolefin resin [A] and soft polymer component.

[0119]

And, to improve the crosslinking efficiency, it is desirable to add a compound having two or more radically polymerizable functional groups in the molecule in case of treating with an organic peroxide, because it can yield a heat-shrinkable sheet or film with excellent impact resistance (film impact).

[0120]

Examples of the compounds having two or more radically polymerizable functional groups in the molecule are divinylbenzene, vinyl acrylate, and vinyl methacrylate. The amount of such compound to be added is no more than 1 weight part, preferably 0.1 - 0.5 weight part, per 100 weight parts of the combined amount of cycloolefin resin [A] and the soft polymer (17).

[0121]

When 0.01 - 40 weight parts, preferably 0.05 - 30 weight parts (0.1 - 20 weight parts are even better), of such soft polymer [soft (co)polymers (i) - (v)] is used for each 100 weight parts of the cycloolefin resin [A], a heat-shrinkable sheet or film with

excellent shrinking property (heat shrinkability), waterproofness, chemical resistance, tearability, transparency, and high rigidity, can be inserted easily with the content when it is used as a heat-shrinkable film, and well-balanced properties, can be obtained.

[0122]

[Other additives]

The heat-shrinkable sheet or film of this invention comprises the above-described cycloolefin resin [A], and if necessary, the above-described "other resin components". However, in addition to these components, conventional heat stabilizer, anti-weather stabilizer, antistatic, slipping agent, anti-blocking agent, fog inhibitor, lubricant, dyes, pigments, natural oil, synthetic oil, and/or wax may be added.

[0123]

Examples of the stabilizer to be added as voluntary component are phenolic antioxidants such as TETRAKIS[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] methane, alkyl β -(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 2,2'-oxamido-BIS[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and so on; metallic salts of aliphatic acids such as zinc stearate, calcium stearate, calcium 1,2-hydroxystearate and so on; and esters of aliphatic acid and polyvalent alcohols, such as glycerin monostearate, glycerin distearate, pentaerythritol monostearate, pentaerythritol distearate, pentaerythritol tristearate and so on. Each of these compounds may be added alone, or they may be combined and added together. Example is the combination of TETRAKIS[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] methane and zinc stearate and glycerin monostearate. One, two or more such stabilizers may be used together.

[0124]

And, silica, kieselghur, alumina, titanium oxide, magnesium oxide, pumice powder, pumice balloon, aluminum hydroxide, magnesium hydroxide, basic magnesium carbonate, dolomite, calcium sulfate, potassium titanate, barium sulfate, calcium sulfite, talc, clay, mica, asbestos, glass fibers, glass flakes, glass beads, calcium silicate, montmorillonite, bentonite, graphite, aluminum powder, molybdenum sulfide, boron fibers, silicon carbide fibers, polyethylene fibers, polypropylene fibers, polyester fibers, polyamide fibers and so on can be mentioned as the examples of organic and inorganic fillers.

[0125]

Any known methods can be employed as the method to mix the cycloolefin resin of this invention with other components. For example, components can be mixed simultaneously.

[0126]

Cycloolefin polymer and other components can be mixed by any known methods. For example, components can be mixed simultaneously.

[Preparation of heat-shrinkable sheet or film]

The cycloolefin resin [A] (or resin composition containing such resin [A]) prepared in the above-described manner is formed into a sheet or a film by using a known method such as T-dies process, inflation process, or press molding process, and then the sheet or film is stretched monoaxially or biaxially (biaxial stretching is preferred), to obtain the heat-shrinkable sheet or film of this invention. Thickness of the heat-shrinkable sheet or film of this invention can be set appropriately, based on its application.

[0127]

In case of stretching the unstretched sheet or film monoaxially or biaxially, the unstretched sheet or film is heated and stretched at a temperature higher than the glass transition temperature (Tg). In this invention, stretching ratio can be set appropriately, by taking the property of the sheet or film, such as the required strength into consideration. As to the stretching method, any known stretching methods such as roll stretching process, tenter stretching process, or inflation process can be used.

[0128]

Preferred preparation method of the heat-shrinkable sheet or film of this invention is explained further in the following examples. Thus, first the cycloolefin resin [A] or the resin composition containing [A] prepared in the above-described manner is used to prepare a sheet or a film having a thickness of, for example, 0.01 - 2 mm, by using T-dies molding process or inflation molding process.

[0129]

Then, the thus-prepared sheet or film is heated at a temperature 0 - 60°, preferably 10 - 40°C, higher than the glass transition temperature (Tg) of the resin [A] (or the

resin composition containing [A]) that forms the sheet or film. Then, the heated sheet or film is stretched 1.5 - 10-folds in longitudinal direction and lateral direction sequentially or simultaneously to both directions, to obtain a biaxially stretched heat-shrinkable sheet or film that has a thickness of 1 - 100 μm , preferably 10 - 50 μm . Heat shrinking ratio (%) of thus-obtained heat-shrinkable sheet differs with the type of cycloolefin resin [A] or the resin composition containing such resin [A] and the temperature ($^{\circ}\text{C}$) being employed for the heat treatment. But, if the cycloolefin resin [A] or the resin composition containing such resin [A] is treated, for example, at 80 - 120 $^{\circ}\text{C}$, the heat shrinking ratio will be about 20 - 70%.

[0130]

In case of forming a heat-shrinkable sheet or film made from the resin composition containing such cycloolefin resin [A] in this invention, the "polymers (1) derived from the hydrocarbons containing one or two unsaturated bonds (polyolefin)" or the above-described "soft polymer (17)" are used preferentially. Among them, the above-said " α -olefin copolymer (ii)" is particularly preferred because they can give a heat-shrinkable sheet or film that excels in film impact and can give a well balanced shrinking property, transparency, tensile strength, tear strength, gas permeability, and water vapor permeability.

[0131]

And, the third heat-shrinkable sheet or film of this invention can be prepared by properly utilizing the method known in the prior art. For example, the above-described cycloolefin resin [A] and the above-described other resins are molten and co-extruded into forming a sheet, and subsequently the sheet is stretched monoaxially or preferably biaxially in such a way to give a proper stretching ratio and thickness. And, for example the cycloolefin resin [A] sheet or film obtained by the above-described method is laminated with other resin sheet or film, and they are heated and pressed to form a sheet of laminate which may be stretched in the above-said manner.

[0132]

The thus-obtained heat-shrinkable sheet or film of this invention excels in shrinking property, waterproofness, chemical resistance, tearability, and transparency, and has high rigidity and can be inserted easily with the content when it is used as a heat-shrinkable film. Furthermore, this heat-shrinkable sheet or film excels also in the balance of such properties.

[0133]

The thus-obtained heat-shrinkable sheet or film of this invention is suitable for various applications such as storage of foods, chemicals, tools, and notes; as a heat-shrinkable packaging material for shipment; as a sealable packaging material for sealing a cap or as a plug, etc; and as heat-shrinkable labeling material for bottles and containers and so on.

[0134]

[Effect of invention]

As explained above, the heat-shrinkable sheet or film of this invention excels in shrinking property and waterproofness, and can be torn easily. Due to such property, the heat-shrinkable sheet or film of this invention is useful for various shrinkable films, and it excels also in visibility of the content after packaging and protecting ability.

[0135]

[Examples]

This invention is explained further by way of the following examples which, however, are not intended to limit the scope of this invention.

[0136]

Methods of testing the properties and methods of evaluation in this invention are illustrated in the following.

(1) Melt flow index (MFR) :

Measurement was taken at a certain temperature (T°C) under a load of 2.16 kg, by following the procedure specified in ASTM-D1238.

(2) Softening temperature (TMA) :

Softening temperature (TMA) was measured by the thermal deformation behavior of a sheet (thickness = 1 mm), using the Thermomechanical Analyzer manufactured by Du Pont Co.. A quartz needle was placed over the sheet and a load 49 g was applied. Temperature was raised at a rate of 5°C/minute. The temperature at which the needle invaded 0.635 mm was regarded as the TMA.

(3) Glass transition temperature (Tg) :

Glass transition temperature was measured by raising the temperature at a rate of 10°C/minute, using DSC-20 manufactured by Seiko Denshi Kogyo K.K..

(4) Haze :

Haze was measured by the procedure specified in ASTM-D1003.

(5) Tensile strength :

A dumbbell type piece (ASTM, type IV) was punched out from the foamed molded article obtained in the examples, and tensile strength was measured at 23°C by the procedure specified in ASTM-D638.

(6) Film impact (impact strength) :

A test piece (100 x 100 mm) was cut out from the molded article, and impact strength was measured, using a Film Impact Tester manufactured by Toyo Seiki K.K. Diameter of the impact head was 1 inch.

(7) Tear strength :

Test strength was measured by Ermendorff tear method, following the procedure specified in JIS Z1702. Temperature at which measurement was taken was 23°C.

(8) Shrinking property :

A rectangular piece (length = 150 mm, width = 20 mm) was cut out from the molded article, and lines (marker) were drawn at 100 mm interval in the longitudinal direction. The test piece was set at the temperature illustrated in Fig. 1, and the length of the tangent line after shrinkage was measured at 5 minutes interval. Based on the distance between the marked lines before and after the test, shrinking ratio was calculated, using the following formula.

[0137]

Shrinking ratio (%)

$$\begin{aligned} &= \{[\text{Length of marker before the test} - \text{Length of marker} \\ &\quad \text{after the test}]/[\text{Length of marker before the test}]\} \\ &\quad \times 100 \end{aligned}$$

[0138]

(9) Gas permeability :

Oxygen gas permeability : Oxygen gas permeability was measured by using the Model OX-TRAN 100 oxygen gas permeability tester manufactured by Modern Control Co..

[0139]

CO₂ gas permeability : CO₂ gas permeability was measured by using a model PERMATRAN C-IV CO₂ permeability tester manufactured by Modern Control Co..

(10) Water vapor permeability :

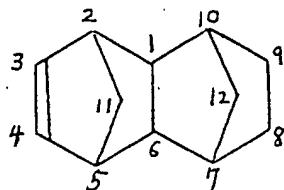
Water vapor permeability was measured with a model PERMATRAN W-600 Water Vapor Permeability tester manufactured by Modern Control Co., at 40°C and 90% relative humidity.

[0140] - [0142]

Example 1

Copolymer [ethylene content measured by C¹³-NMR = 68 mol %, limit viscosity $[\eta]$ measured at 135°C in decalin = 0.65 dl/g, softening temperature (TMA) = 90°C, glass transition temperature (Tg) = 80°C] made of ethylene and 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydro naphthalene (i.e. tetracyclo[4,4,0,1^{2,5(7)},1^{7,10}]3-dodecene, or TCD) (see the following structural formula) was used as the cycloolefin copolymer.

[Chemical formula 16]



It was extruded by an extruder (30 mm ϕ) to prepare a sheet (thickness = 100 μm) by T-dies process. This sheet was stretched biaxially at a stretching ratio of 2 x 2 at 110°C, to prepare a stretched film (thickness = 25 μm). Thus-obtained film was used as the test sample, and its properties were determined.

[0143]

Results are presented in Table 1 and Fig. 1.

[0144]

Example 2

After mixing the pellets 3.4 kg of the random copolymer made of TCD and the ethylene being used in Example 1 and the pellets 0.6 kg made of ethylene/propylene random copolymer (ethylene content = 80 mol %, glass transition temperature (T_g) = -54°C, limit viscosity $[\eta] = 2.2 \text{ dl/g}$), a film (thickness = 25 μm) was prepared by the procedure of Example 1. Thus-obtained film was used to prepare a test sample, and its properties were determined.

[0145]

Results are illustrated in Table 1 and Fig. 1.

[0146]

Example 3

Procedure of Example 2 was followed, except using ethylene/4-methylpentene-1/random copolymer (4-methylpentene-1 served as the comonomer, density = 0.915 g/m^3 , MFR measured at 190°C and 2.16 kg load = 2.0 g/10 minutes) to replace the rubber component.

[0147]

Results are illustrated in Fig. 1 and Fig. 1.

[0148]

[Table 1]

Table 1

	<u>Example 1</u>	<u>Example 2</u>	<u>Example 3</u>	
Haze (%)	0.2	40	17	
<u>Tensile strength (Longitudinal/lateral)</u>				
Stress at breaking point (Kg/cm ²)	550	350	450	
Elongation at breaking point (%)	5	9	8	
Elastic modulus (Kg/cm ²)	27000	20000	22000	
Film impact (kg.cm/cm)	23°C 0°C	300 300	3500 3000	2300 2100
Tear strength (longitudinal/lateral)(kg/cm)	-	5/5	5/5	
Gas permeability (cm ³ .mm/m ² .24 hr.atm)	CO ₂ O ₂	60 25	95 30	90 35
Water vapor permeability (g.mm/mm ² .24 hrs)	0.09	0.13	0.11	

Brief explanation of drawing

[Fig. 1] Fig. 1 is a graph to illustrate the relation between the temperature (°C) employed for heat treatment and the shrinking ratio (%) when the heat-shrinkable films described in Examples 1 - 3 were subjected to heat treatment while changing the temperature in 50°C - 120°C range by 10°C increment. In Fig. 1, abscissa indicates the temperature (°C) employed for heat treatment, and ordinates indicates the shrinking ratio (%).

Fig. 1

Shrinking property

